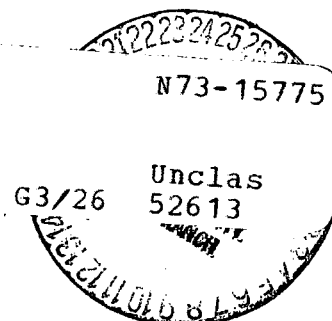# USE OF THE CHARACTERISTIC X-RAY TEMPERATURE OF VANADIUM FOR THE ESTIMATION OF INTERATOMIC BONDS IN ITS CRYSTAL LATTICE

V.P. Mikhal'chenko and V.B. Lototskiy

USE OF THE CHARACTERISTIC X-RAY TEMPERATURE OF VANADIUM FOR THE ESTIMATION OF INTERATOMIC BONDS IN ITS CRYSTAL LATTICE

V. P. Mikhal'chenko, V. B. Lototskiy

ABSTRACT: A formula is given for calculating the intensity of elastic and inelastic X-ray scattering in the crystal lattice of vanadium. Experimental measurements and calculations based on this formula show that the characteristic X-ray temperature of vanadium is practically insensitive to interactions between remote atoms and to off-center interactions in its crystal lattice.

Approximation of the vibrational spectrum of a crystal by a Debye parabola is some- /1300* times acceptable for estimating some of the dynamic characteristics of solids. This means that for such estimates it is necessary to know a single parameter—the Debye characteristic temperature θ. The values of θ can be determined from a whole series of physical measurements: the specific heat θ_C, the velocity of sound θ_S, the electrical resistance θ_R, the Mossbauer effect probability θ_M, the intensities of elastically or inelastically scattered x-rays θ_X, the scattering of electrons θ_e or of thermal neutrons θ_n.

Small differences between the effective values of θ of a given crystal, determined by these physical methods, are quite reasonable. These discrepancies are caused (in addition to the different nature of the averagings) both by the selective sensitivity of the corresponding physical properties of the crystal to the form of the spectral distribution of vibrational frequencies (identical to the Debye model only at the lowest frequencies), and also by the anharmonicism of the lattice vibrations.

Since the error, introduced in the concept of the Debye-Waller M factor with the attractive feature of a one-parameter spectrum, is less than the errors introduced in the concept of other physical properties of the crystal that depend explicitly or implicitly on the spectrum [1], the quantity θ_X, associated with the M factor, has been interpreted by many authors as a measure of the interatomic bonds in a lattice. This has been the subject of discussions during the last fifteen years [2-9]. Without an elaborate analysis of the different viewpoints, one can, however, proceed to the question of θ_X as a measure of the interatomic bonds from a quantitative aspect.

Actually, up to the present time considerable information has been accumulated on the phonon spectra of crystals of cubic as well as noncubic systems. This makes it possible to calculate the value of θ_X of a given crystal directly, taking into consideration the actual and modeled frequency distribution functions $f(\omega)$ of the normal vibrations and, thus, to estimate the effect of different interactions in the lattice on the

---

*Numbers in the margin indicate pagination in the foreign text.

quantity* θ_X.

Such a procedure for calculating θ_X is performed in this paper for vanadium since the phonon spectroscopy of this metal has been the subject of extensive theoretical and experimental research (neutron diffraction as well as quite recent x-ray diffraction studies [11]).

To calculate θ_X for vanadium we used the f(ω) function calculated theoretically with the aid of the following models: 1) by the method of superposition of the Debye and Einstein spectra [12]; 2) the Born-Karman model, taking into consideration central interaction in the first two coordination spheres and off-center interaction of the nearest neighbors [13]; 3) the Fine model [14]; 4) the Bhatia model [15]; 5) the De-Launay model [16].

Besides the theoretically computed f(ω) functions, we used the phonon spectra reconstructed from neutron diffraction data, i.e., without any modeled concepts: 6) in [17]; 7) in [18]; 8) in [19], as well as the f(ω) reconstructed from experimental data on the one-phonon thermal diffuse scattering of x-rays in [11]; 9) with interactions up to the seventh coordination sphere taken into consideration; 10) with "interplanar" interactions (in addition to method 9) taken into consideration.

The values of θ_X were calculated from the formula

$$\theta_X^2 = \frac{1}{3}\left(\frac{k}{h}\right)^2 \int_0^{\omega_m} \omega^{2} f(\omega)\, d\omega \Big/ \int_0^{\omega_m} f(\omega)\, d\omega,$$

where h is Planck's constant, divided by $2\pi°$.

The calculations were performed by a numerical graphical method similar to that of [20]. The graphical representation of the f(ω) functions for methods 2-5 is obtained by smoothing the corresponding f(ω) histograms given in [21], and for method 1—by using the vanadium elasticity constants determined by the ultrasonic pulse method in [22]. The graphical representation of f(ω) for methods 6-8 is borrowed from [17-19], and for methods 9 and 10—from [11]. The results of the calculation of θ_X for $300°$ K by the above-listed methods are presented below**. (For comparison we also give the values of θ_c and θ_s from [20], as well as θ_n, calculated in [23] from the temperature dependence of the elastic noncoherent scattering of neutrons by polycrystalline vanadium.) The calculated results were as follows: 381 (method 1), 377 (method 2), 373 (method 3), 385 (method 4), 374 (method 5), 340 (method 6), 362 (method 7), 325 (method 8), 367 (method 9), 374 (method 10): $\theta_s = 389$; $\theta_c = 425$ and $\theta_n = 366$ (in $°$K).

---

*We identify the values of θ_X as those determined from elastically and inelastically scattered x-ray data. A rigorous proof of this is given in [10].

**Here θ_{Xi} (i = 1, 2, ..., 10) means the value of θ_X, calculated from the phonon spectra by methods 1-10, respectively.

2

It is seen from these data that the maximum difference between θ_{Xi} (i = 1-5) values is only 13^0K. Bearing in mind the theoretical models of methods 1-5, one can state that at least central interaction in the first and second coordination spheres has a significant effect on the value of θ_X.

The discrepancies between the values of θ_{Xi} (i = 6-8), where the maximum difference was $\Delta\theta_X = 37^0$K, were somewhat unexpected. This means, first of all, that θ_X is extremely sensitive to the shape of the phonon spectrum at low frequencies. In fact, the presence of a well-pronounced maximum, caused (according to the interpretation of [19]) by the Cohen effect, at the lowest frequencies of f(ω) drastically lowers the value of θ_{X8} compared to θ_{X7}, calculated from the f(ω) reconstructed in [18], where this maximum is not found. In addition, the high sensitivity of θ_X to the initial portion of the spectrum is evident in the fact that even a small inaccuracy in the parabolic extrapolation from frequencies of the order of $0.2\omega_{max}$ to $\omega = 0$ for the function f(ω), reconstructed in [17], causes a difference $\theta_{X7} - \theta_{X6} = 22^0$K, which was pointed out in our paper*[20].

With respect to the values θ_{X9} and θ_{X10}, their difference $\theta_{X10} - \theta_{X9}$ is 7^0K, despite the marked differences at high frequencies in the f(ω) functions shown in Figs. 9 and 10 of [11]. It should be remembered here that in the method 1 model only central interaction in the first and second coordination spheres is considered.

Thus, from an analysis of the data one can conclude that the X-ray characteristic temperature θ_X is practically insensitive to interactions with remote neighbors (third nearest and more remote) and also to off-center interactions in the crystal lattice. At the same time θ_X, being an overall characteristic, is a convenient parameter for the estimation of bond tightness ($\sim m\theta_X^2$), at least for interactions between nearest and se second nearest neighbors in the lattice of crystals with cubic symmetry.

An analogous approach to a discussion of θ_X of noncubic crystals, although complicated by the tensor nature of the Debye-Waller M factor, can be the subject of a separate paper.

In conclusion it must be noted that all ten calculated values of θ_{Xi} (as well as θ_n) are systematically less than θ_c and θ_s. This agrees with the conclusions of [25, 26], where it is shown that the inequality $\theta_X < \theta_s \cong \theta_s$ is a fairly universal property of solids, if their atomic structure is taken into consideration.

REFERENCES

1. Blackman, M. Handbuch Phys., Springer, 1955, 7, 325.
2. Zvyagina, A. P. and Iveronova, V. I., Fiz. Tverd. Tela, 1960, 2, 118.

*It is interesting to note that θ_{X6}, calculated in [24], was found to be equal to 323^0K, which is probably associated with some arbitrariness in the low-frequency extrapolation.

3. Kagan, A. S. and Umanskiy, Ya. S., Fiz. Tverd. Tela, 1961, 3, 2683.
4. Iveronova, V. I., Zvyagina, A. P. and Aybinder, B. Yu., Fiz. Metallov Metallvedeniye, 1962, 14, 141.
5. Potapov, L. P., Author's abstract of candidate's dissertation. TsNIIChM, Moscow, 1964.
6. Mikhal'chenko, V. P. Tezisy doklada VIII Vsesoyuznogo soveshchaniya po primeneniyu rentgenovskikh luchey k issledovaniyu materialov (Proceedings of VIII All-Union Conference On the Application of X-Rays to Materials Research), Nauka Press, Leningrad, 1964, p. 18.
7. Garber, R. I. and Gindin, I. A., Usp. Fiz. Nauk, 1960, 70, 57.
8. Iveronova, V. I. and Katsnel'son, A. A., Zavodskaya Laboratoriya, 1961, 11, 354.
9. Herbstein, F. H., Advances Phys., 1961, 10, 313.
10. Borie, B., Acta Cryst., 1961, 14, 566.
11. Colella, R. and Batterman, B. W., Phys. Rev., 1970, B1, 3913.
12. Leibfried, G. and Brenig, W., Z. Phys., 1953, 134, 451.
13. Born, M. and Karman, T., Z. Phys., 1912, 13, 297.
14. Fine, P. C., Phys. Rev., 1939, 55, 355.
15. Bhatia, A. B., Phys. Rev., 1955, 97, 363.
16. De-Launay, J., Solid State Phys., 1956, 2, 220.
17. Stewart, A. T. and Brockhouse, B. N., Rev. Mod. Phys., 1958, 30, 250.
18. Chernoplenkov, N. A., Zemlyanov, M. G., Chicherin, A. G., and Lyashchenko, B. G., Zh. Eksp. Teor. Fiz., 1963, 44, 858.
19. Page, D. J. Proc. Phys. Soc. (London), 1967, 91, 76.
20. Mikhal'chenko, V. I. and Lototskiy, V. B., Fiz. Metallov Metallovedeniye, 1969, 28, 552.
21. Pelach, I., Haas, R., Kley, W., Krebs, K. H., Peretti, J., and Rubin, R., Inelastic scattering of neutrons in solids and liquids, (International Atomic Agency), Vienna, 1963, Vol. II, p. 155.
22. Alers, G. A., Phys. Rev., 1960, 119, 1532.
23. Brockhouse, B. H., Can. J. Phys., 1955, 33, 889.
24. Weiss. R. J. and De Marco, J. J., Phys. Rev., 1965, A140, 1223.
25. Krivoglaz, M. A., Voprosy fiziki metallov i metallovedeniya (Problems in the Physics of Metals and Metallurgy), Press of the Academy of Sciences USSR, Kiev, 1961, p. 35.
26. Blackman, M. Acta Cryst., 1956, 9, 734.